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High-resolution magnetic-resonance spectroscopy of thermal donors in silicon

V.V. Emtsev Jr.[a], C.A.J. Ammerlaan[a,*], A.A. Ezhevskii[b], A.V. Gusev[c]

[a]*University of Amsterdam, Amsterdam, The Netherlands*
[b]*University of Nizhny Novgorod, Nizhny Novgorod, Russia*
[c]*Institute of Chemistry of Highly-Pure Substances, RAS, Nizhny Novgorod, Russia*

Abstract

Oxygen-related thermal donors in silicon form a group of defects with very similar properties. In a magnetic resonance experiment carried out under the normally applied conditions the individual species, up to 16 have been reported, are not distinguished. Due to lack of resolution only an overall integrated signal covering the whole group is recorded. In this paper two independent ways of improving the resolution in magnetic resonance are reported and applied to the Si-NL8 spectrum of the thermal double donors and to the structurally related Si-NL10 center. Line widths of the resonances caused by unresolved hyperfine interactions with the magnetic nuclei of isotope ^{29}Si, nuclear spin $I = 1/2$ and natural abundance 4.7%, are near 0.3 mT. Monoisotopic silicon with the ^{29}Si concentration reduced to 0.09% has been used to observe the Si:P, Si-NL8 and Si-NL10 resonances. In this material a line width as low as 0.045 mT has been observed. The second improvement of resolution is achieved using high-frequency high-field EPR spectrometers at 92 GHz and at 140 GHz for the Si-NL8 spectrum and at 349 GHz for Si-NL10. At these higher frequencies an increase of line structure is achieved by, e.g., a factor 15 when comparing a D band (140 GHz) with a classical X band (9 GHz) experiment. Due to 'g strain' an increase of line width may occur. Under the high-resolution conditions individual species of thermal donors are separated.

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1. Introduction

Magnetic resonance is a spectroscopic technique in which a paramagnetic center is characterized by its specific spectrum. For analysis of the spectrum the powerful concept of spin-Hamiltonian is used. Following such an analysis, a small set of constants, such as g tensor, hyperfine interaction constants, etc., specifies the spectrum. In general the g values alone are sufficient to uniquely identify the center. In other words, no two different centers have the same g tensor. However, there exist exceptions. The most notorious case, may be, is the family of thermal donors in silicon, which consists of at least 16 specific members [1]. These members are very similar in their structure with the consequence that g values are nearly equal. In a standard EPR experiment the differences are too small to be separated. Instead an overall broadened line is observed. The resolution in this case apparently is not large enough. In the paper two independent ways are described to enhance the spectral resolution. The first of them is the use of monoisotopic silicon enriched in the ^{28}Si isotope. The absence of ^{29}Si reduces unresolved hyperfine interactions and leads to narrower lines. Secondly, the application of high magnetic fields increases the splitting between lines with only small difference in their g value. The effect of both improvements is verified on the

*Corresponding author. Sluisvaart 74, 1191 HE Ouderkerk aan de Amstel, The Netherlands. Tel.: +31 20 4963324; fax: +31 20 4967681.
E-mail address: c.ammerlaan@tiscali.nl (C.A.J. Ammerlaan).

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well-known shallow donor phosphorus and applied to obtain species-resolved spectra for the thermal donors and the NL10 centers in silicon.

2. Monoisotopic silicon

In the cases to be considered, with true electron spin $S = \frac{1}{2}$, the line width of the resonance is determined by unresolved hyperfine interactions with the ^{29}Si isotopes, which occur to the abundance of 4.7% in natural silicon and have nuclear spin $I = \frac{1}{2}$. These nuclei are present at random sites as ligands of the paramagnetic center and their hyperfine interaction is probed by the electron in its extended orbit. Due to the hyperfine interaction the resonance field is split in pairs, symmetrically displaced by $\Delta B_l = a_l m_{I,l}/g\mu_B$, with $m_{I,l} = \pm\frac{1}{2}$, with respect to the

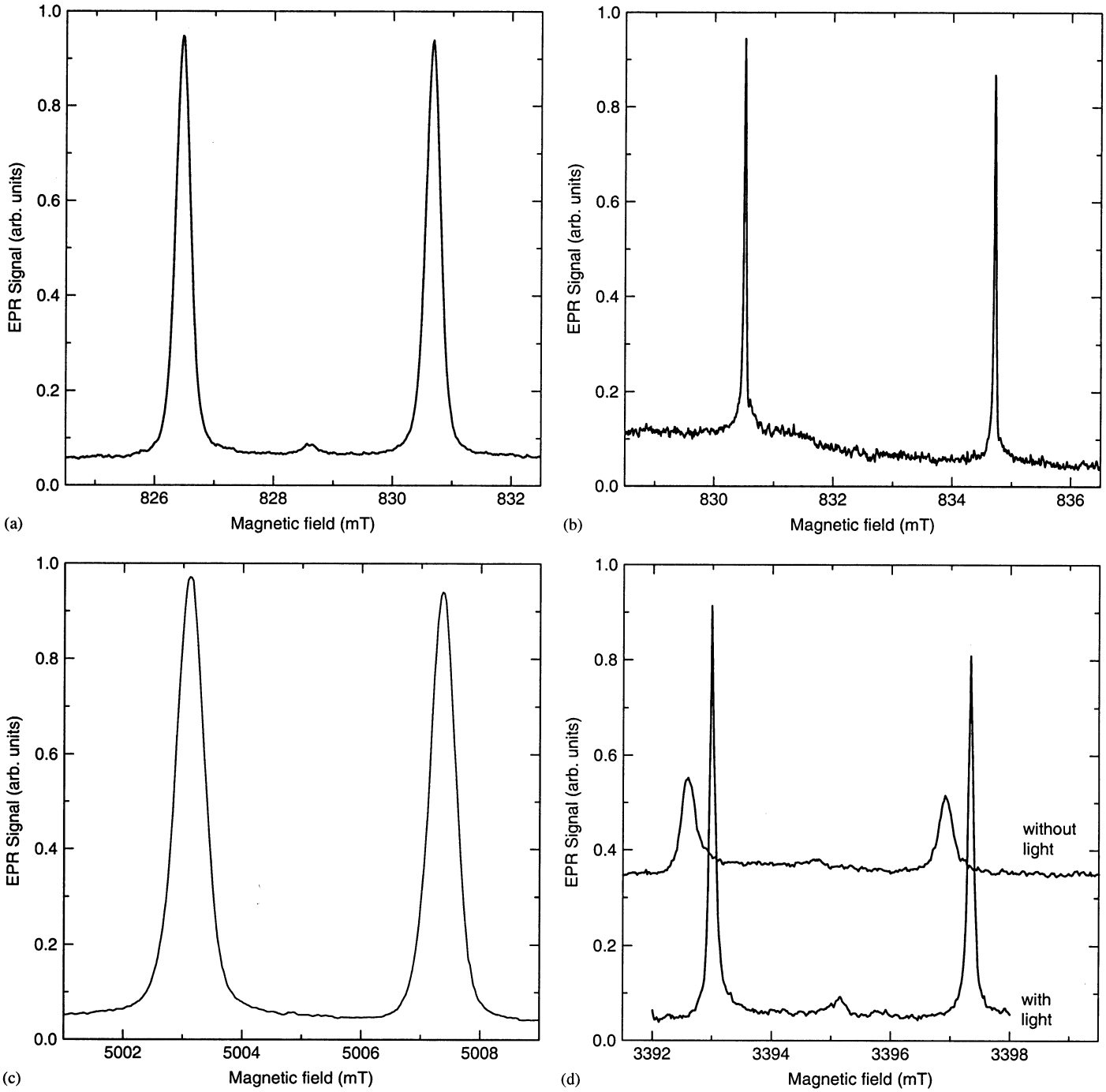

Fig. 1. Electron paramagnetic resonance spectra of phosphorus in silicon. (a) Natural silicon $f = 4.7\%$, microwave frequency $\nu = 23$ GHz, full-width at half-maximum FWHM = 0.29 mT, (b) monoisotopic silicon $f = 0.09\%$, frequency $\nu = 23$ GHz, FWHM = 0.045 mT, (c) natural silicon, frequency 140 GHz, FWHM = 0.50 mT, (d) with and without cavity light, measured at temperature $T = 2$ K, monoisotopic silicon, frequency 92 GHz, FWHM = 0.11 mT (with light).

central position $B_0 = h\nu/g\mu_B$. The line width parameter ΔB is given as the total effect of all ligand sites by $M_2 = \Delta B^2 = \sum_l f(a_l/2)^2/(g\mu_B)^2$, where the summation by index l is over all the interaction sites around the donor position. Here, M_2 is the second moment of the line shape, f the nuclear abundance of the ^{29}Si isotope, and a_l the hyperfine interaction constant. In the case of a Gaussian line shape the full-width at half-maximum (FWHM) equals $2(2\ln 2)^{1/2}\Delta B$ and the width is proportional to $f^{1/2}$. However, the electron distribution does not necessarily lead to a Gaussian line shape. A check on this behavior may be carried out by a calculation of M_4, the fourth moment of the distribution. For a Gaussian shape one requires $M_4/3M_2^2 = 1$, for other shapes, such as Lorentzian, the ratio can deviate appreciably. The dependence on abundance f of isotopes can vary from linear at low to square-root at high concentrations [2]. The line narrowing effect on the phosphorus spectrum from an FWHM $\approx$ 0.3 mT for natural silicon with $f = 0.047$, to FWHM = 0.045 mT for monoisotopic silicon with $f = 0.0009$, is

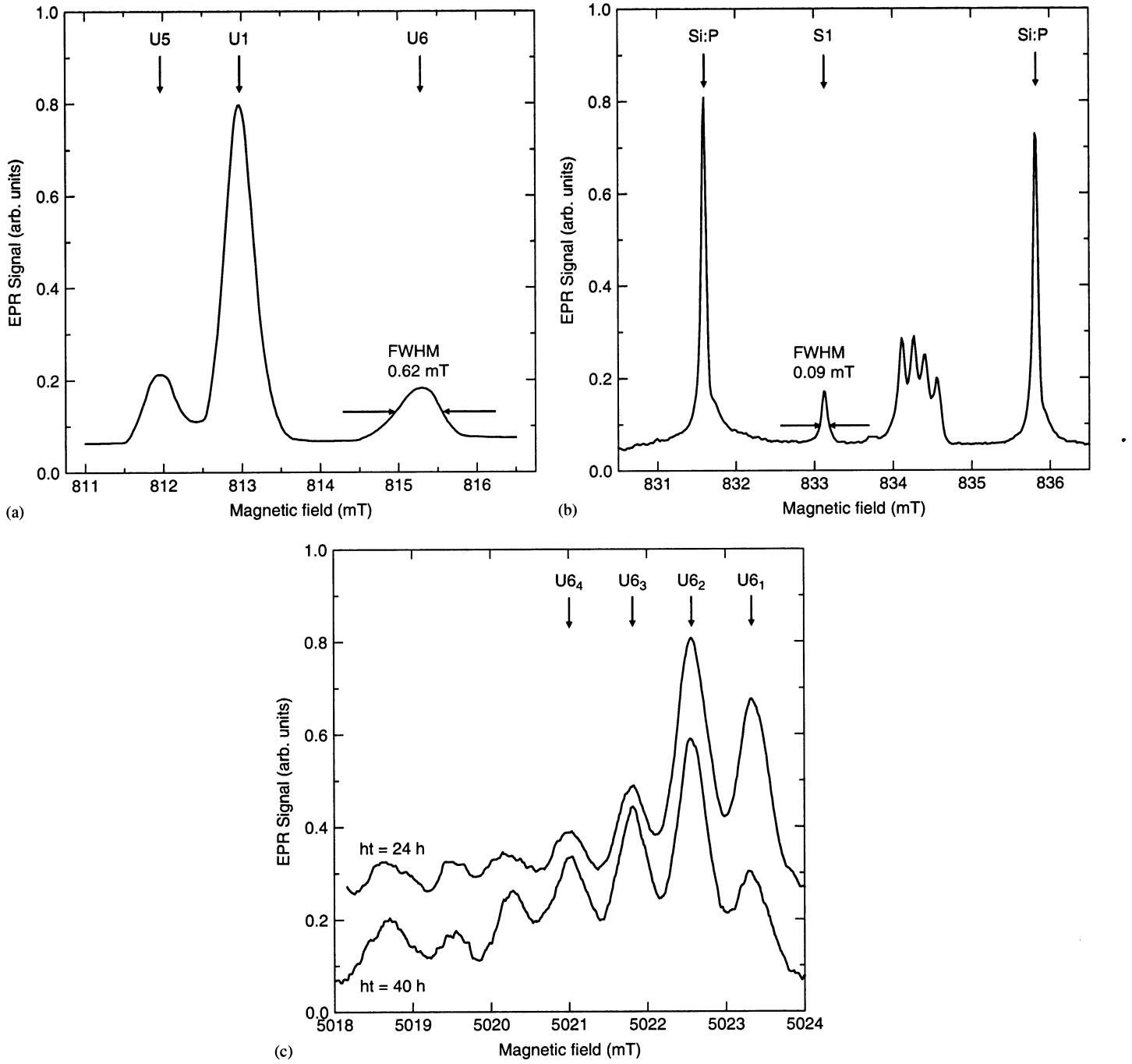

Fig. 2. Electron paramagnetic resonance spectra Si-NL8 of thermal donors in silicon. (a) Spectrum Si-NL8 in natural material $f = 4.7\%$, microwave frequency $\nu = 23$ GHz, $B//[0\,1\,1]$, components U5, U1 and U6 of all orientations of the orthorhombic center, (b) monoisotopic material $f = 0.09\%$, frequency 23 GHz, B near [1 0 0], component S1, (c) natural silicon, frequency 140 GHz, components $U6_1$, $U6_2$, $U6_3$ and $U6_4$.

shown in Figs. 1(a) and (b). The resonance lines have a Gaussian shape and the width behaves closely to a square-root dependence on f [3]. For the thermal donor the isotope broadening is interwoven with the species-dependent inhomogeneous broadening and cannot be shown separately. Nevertheless, the line observed for a field B in the [1 0 0] direction, where all species are believed to have nearly equal g value, is substantially narrower than for the spectral lines with B//[0 1 1]. The illustration is given in Figs. 2(a) and (b).

3. High-field high-frequency EPR

At high magnetic field, the Zeeman splitting between levels with different m_S will be larger, proportional to the field. It will create the more favorable conditions for the separation of transitions with similar Zeeman splitting factors g. Following the resonance condition one can write $\delta B = -(h\nu/g^2\mu_B)\delta g$ and conclude that the resolution will be proportional to the operating frequency ν of the spectrometer. In Figs. 1(c) and (d) the results are shown for measurements at 140 and 92 GHz of the phosphorus resonance on natural and monoisotopic silicon, respectively. In comparison to the low-frequency measurements at 23 GHz, Fig. 1(a), a modest increase of line width in the natural silicon sample to about 0.5 mT is observed. This effect, usually referred to as g strain, can reflect a homogeneous broadening of all individual resonances, e.g., due to saturation at low temperatures, short life times at high temperatures, too high microwave power, or too large modulation field. Fig. 1(d) shows that reduction of spin-lattice relaxation time by sample illumination can have a substantial effect on the observed line width. Passage conditions in recording the resonance must be optimized. Line widths can also increase as the result of a distribution of g values among the individual paramagnetic centers as an inhomogeneous effect. It can be due to a different environment of each paramagnetic center leading to complexes with a remote other center and some distribution in g values, or simply due to unsatisfactory uniformity of the magnetic field over the sample volume. In comparing Figs. 1(c) and (a) one must conclude that increase of frequency had an adverse effect on the separation of the phosphorus hyperfine lines.

In early EPR measurements on thermal donors at frequency 23 GHz the resolution of species was not achieved. It was only observed that upon prolongation of heat treatment at the thermal donor formation temperature of 450 °C the g tensor was shifting towards more isotropic character [4]. Thermal donors are centers with an orthorhombic-I symmetry. The principal values of the g tensor are found in the [1 0 0] and two perpendicular [0 1 1] directions. The shift appeared nearly exclusively for the smaller g value in the [0 1 1] direction, the two other principal g values did not show noticeable shift. The shift was interpreted as due to the gradual development of later species with more isotropic structure in the thermal donor

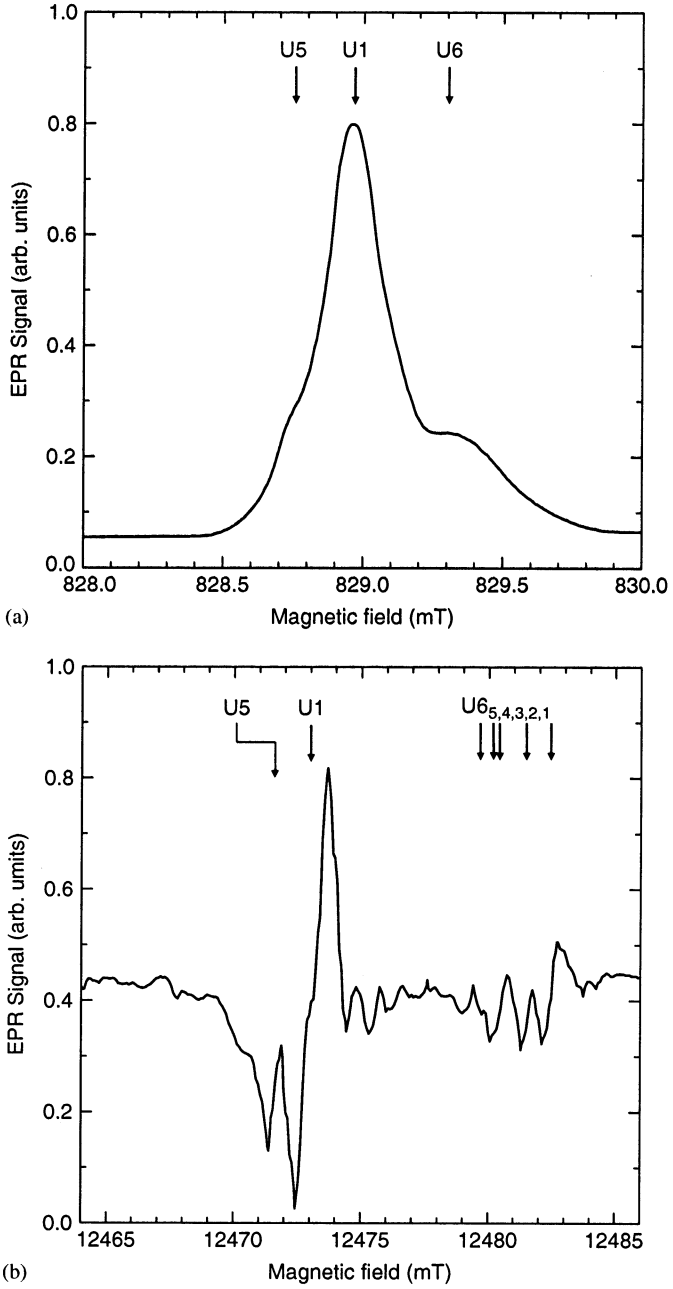

Fig. 3. Electron paramagnetic resonance spectra of Si-NL10 centers related to thermal donors, showing components U5, U1 and U6 of all orientations. (a) Spectrum Si-NL10 in natural material $f = 4.7\%$, frequency $\nu = 23$ GHz, B//[0 1 1], (b) natural silicon, frequency $\nu = 349$ GHz, B//[0 1 1].

formation treatment. At high frequencies it has been possible to resolve the individual resonance of species for the [0 1 1] direction with the largest species dependence. A result is shown in Fig. 2(c) for the thermal donor spectrum Si-NL8 measured in the 140 GHz spectrometer. The envelope taken over species resembles the asymmetric shape of resonance U6 as shown in Fig. 2(a). Its width has increased by factor ≈ 6 from 0.62 mT at 23 GHz to about 4 mT at 140 GHz, i.e., proportional to the applied magnetic field, identifying the spread between species as a Zeeman

effect. Upon increase of heat treatment time from 24 to 40 h the individual species do not change their resonance field. Only their relative intensities change, e.g., species $U6_1$ lowers in intensity whereas $U6_4$ becomes stronger. This behavior corresponds to the overall shift of the U6 resonance towards lower field and more isotropic behavior. Resonances of individual species are about 0.5 mT wide, equal to the width of phosphorus lines at 140 GHz shown in Fig. 1(c). It provides the evidence that further inhomogeneous structure in these resonances is absent. The center NL10 has an about four times less anisotropic spectrum and even in the [0 1 1] direction of largest anisotropy the components of different defect orientations U5, U1 and U6 are far from ideally resolved, as shown in Fig. 3(a). For its resolution a still higher field is required. The spectrum with separated species, again for the more sensitive [0 1 1] direction, measured at 349 GHz is shown in Fig. 3(b). The observation of species character for both the NL8 and NL10 centers further corroborates the relation in their structure. EPR center NL10 has been identified as a hydrogenated thermal donor [5]. By analysis of the angular variation of resonances the g tensor of some species of the NL8 thermal donors and the related center NL10 were obtained [6].

4. Conclusion

Both ways of improving the resolution in the spectrum, (1) reduction of line width from about 0.3 to 0.05 mT by using silicon from which the isotope ^{29}Si has been removed, and (2) increasing of line splitting proportional to the frequency using a high-field high-frequency EPR spectrometer, give the expected beneficial result. Under improved conditions individual components in the thermal donor spectrum are observable. Their g tensors can be determined. Both for the NL8 and the NL10 center the species character is demonstrated confirming their close relationship.

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